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## APPENDIX

### PROPOSED STANDARDIZATION OF THE SULPHUR BOILING POINT

All experimental work published has been drawn upon in preparation of these specifications. The specifications relate to apparatus and procedure suitable for the standardization primarily of resistance thermometers and thermocouples, and it was therefore considered permissible to limit the type of apparatus somewhat closely. The aim has been to impose conditions which are sufficient to insure that the thermometer shall assume a definite temperature, dependent only upon the pressure, when placed in the apparatus, and the question as to whether these conditions are really necessary has received only secondary consideration. Thus the question as to the temperature attained in tubes larger or smaller than those specified need not be considered. It may further be supposed that the thermometer or couple will be mounted in a protecting tube or sheath, and that the diameter of such a tube or width of the sheath will be less than 2 cm.

The specifications relate to the following matters: (1) Boiling apparatus, (2) purity of sulphur, (3) radiation shield, (4) procedure, and (5) computations.

(1) *Boiling Apparatus*.—The boiling tube is of glass, fused silica or similar material, and has an internal diameter of not less than 4 nor more than 6 cm. The length must be such that the length of the vapor column measured from the surface of the liquid sulphur to the level of the top of the insulating material surrounding the tube shall exceed the length of the thermometer coil by at least 20 cm.<sup>11</sup> Heating is by any suitable heater at the bottom of the tube, and the arrangement must be such that the heating element, and all conducting material in contact with it, terminate at least 4 cm below the level of the liquid sulphur. If a flame is allowed to impinge directly on the tube, the heat insulation must extend at least 4 cm below the level of the liquid sulphur. There should be a ring of insulating material above the heater, fitting the tube closely, to prevent superheating of the vapor by convection currents outside the tube. Above the heater the tube is surrounded with insulating material, not necessarily in contact with it, and of such character as to provide heat insulation equivalent to a thickness of not less than 1 cm of asbestos. The length of this insulation has already been specified. Any device used to close the top of the boiling tube must allow a free opening for equalization of pressure.

(2) *Purity of Sulphur*.—The sulphur should contain not over 0.02 per cent of impurities. It should be tested to determine whether selenium is present.

(3) *Radiation Shield*.—The radiation shield consists of a cylinder open at both ends and provided with a conical umbrella above. The cylindrical part is to be 1.5 to 2.5 cm larger in diameter than the protecting tube of the thermometer, and at least 1 cm smaller than the inside diameter of the boiling tube. The cylinder should extend 1.5 cm or more beyond the coil at each end. The umbrella should fit the thermometer tube closely, should overhang the cylinder, and be separated from the latter by a space 0.5 to 1 cm high. The inner surface of the cylinder must be a poor reflector, such as sheet iron, blackened aluminum, asbestos, or a deeply corrugated surface.

<sup>11</sup> This length was arrived at as follows: The minimum distance from the liquid surface to the bottom of the shield was taken as 6 cm, excess of length of shield over length of thermometer coil 6 cm, distance available for displacing thermometer 6 cm, and minimum distance from top of shield to level of top of insulation 2 cm.

(4) *Procedure*.—The sulphur is brought to boiling <sup>12</sup> and the heating is so regulated that the condensation line is sharply defined and is 1 cm or more above the level of the top of the insulating material. The thermometer, inclosed in its shield, is inserted into the vapor, taking care to have the thermometer coil properly located with respect to the shield, and the thermometer and shield centered in the boiling tube. After putting the thermometer into the vapor time must be allowed for the line of condensation again to reach its proper level. Simultaneous readings of the temperature and barometric pressure are then made. In all cases care should be taken to prove that the temperature is not affected by displacing the thermometer 2 or 3 cm either up or down from its usual position.

(5) *Computations*.—Temperatures are calculated from the pressure by use of the formula,

$$T = 444.60 + 0.0910 (p - 760) - 0.000049 (p - 760)^2$$

If necessary, account should be taken of any difference in pressure between the levels at which the thermometer bulb and the open end of the barometer, respectively, are located. Pressures are to be expressed in the equivalent millimeters of mercury at 0° and under standard gravity ( $g = 980.665$ ).

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<sup>12</sup> If the sulphur has been allowed to solidify in the bottom of the tube, it must be melted from the top downward to avoid breaking the tube. A better procedure is that recommended by Rothe (*Z. S. für Instrk.*, 23, p. 366, 1903), viz, on completing work with the apparatus it is turned so that the tube makes an angle of 30° or less with the horizontal, so that the sulphur on solidifying extends along the sides of the tube, in which position it may be melted down with less danger of breaking the tube. Even when the procedure recommended is followed, breakage of tubes may be reduced by carefully melting the sulphur from the top downward over a bunsen burner before applying heat to it in the apparatus.

WASHINGTON, January 22, 1919.



# A STANDARDIZED METHOD FOR THE DETERMINATION OF SOLIDIFICATION POINTS, ESPECIALLY OF NAPHTHALENE AND PARAFFIN

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## I. INTRODUCTION

Inquiries which the Bureau has received from time to time concerning a standard method for making freezing-point determinations of substances such as naphthalene and paraffin have made it evident that there is little uniformity in the methods used for such work in the industries. This conclusion has been confirmed by an inspection of Treasury Decisions,<sup>1</sup> in which one finds disputes arising out of a failure of industrial laboratories to agree among themselves or with the customs laboratories as to the methods that should be used in obtaining solidification-point determinations of naphthalene, which under a law of 1916 will be admitted free of duty if its solidification point is below 79° C. Naphthalene solidifying at or above this temperature is classified as refined.

The need for such a standard method and apparatus resulted in the calling of a conference of officials of the Customs Service at

<sup>1</sup> Treasury Decisions, 35, Oct. 24, 1918; No. 7 (T. D. 37790-G. H. 8197), p. 5.

the Bureau of Standards to discuss this question. This conference,<sup>2</sup> held in December, 1917, at the Bureau, made certain recommendations in regard to a standard method for obtaining the freezing point of naphthalene. The conference recommended a method which has long been in use in physical-chemical work, namely, the constant-temperature method. The details of the method as applied to determinations of the solidification point of naphthalene and other substances will be described later.

## II. PRINCIPLES UNDERLYING THE CONSTANT-TEMPERATURE METHOD

In general, an impure substance does not have a definite freezing point. For a pure substance the melting and freezing points are identical and either may be defined as the temperature at which crystals and liquid will exist in contact and in equilibrium at standard atmospheric pressure. If a pure liquid is allowed to cool slowly enough, the temperature will be observed to become constant as soon as crystals begin to separate out and will remain constant until all or a considerable part of the substance has solidified.

This constant temperature is often preceded by undercooling, but as soon as crystals form the temperature rises sharply to the freezing point, which may thus be accurately observed. The amount of undercooling which takes place may be greatly diminished by stirring the liquid.

The experimental determination of the freezing point is, therefore, relatively simple if a sufficient quantity of the material is used so that the temperature can be measured by means of a thermometer inserted into it. Melting-point determinations by this method are much more difficult and uncertain than those of freezing point, especially for solids of low thermal conductivity.

If an impure liquid is allowed to cool slowly, the crystals which separate out are, in general, of higher purity than the original

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<sup>2</sup> Those attending this conference were T. D. Simons, Baltimore; D. L. Coburn, Boston; C. C. Roberts, Philadelphia; J. H. Hines, Chicago; E. R. Pickrell, New York; and H. L. Barrick, Washington, from the Treasury Department; and C. E. Waters, E. F. Mueller, R. M. Wilhelm, and J. L. Finkelstein from the Bureau of Standards, Washington.

material, so that the impurities are concentrated in the liquid, which results in a continued lowering of the freezing point as the freezing progresses. If the freezing point of an impure liquid is determined, the temperature will, therefore, not remain constant at any time, but will fall slowly after freezing has begun. It will be noted that the initial freezing point—that is, the temperature observed just after crystals are beginning to form or immediately after undercooling ceases—bears a definite relation to the amount of impurity present. When the freezing point is used as a criterion of purity, the initial freezing temperature is, therefore, the one which is of interest and is by definition called the “freezing” or “solidification” point. In dealing with more or less indefinite mixtures, such as paraffin, the initial freezing point is also by definition taken as the actual freezing point of the substance.

### III. THE CAPILLARY-TUBE METHODS

Among the various methods used to determine freezing or melting points those which make use of a capillary tube of some form are very common. Experiments made here and in other laboratories have demonstrated that the capillary-tube melting-point method will not usually give so consistent nor so accurate results as the constant-temperature method. In special cases, however, when only a small quantity of material is available or when speed rather than accuracy is desired, it may be more satisfactory, or even necessary, to use this less-accurate method.

### IV. PRELIMINARY EXPERIMENTAL WORK

The freezing-point method which will be described was adopted as the result of experimental work done at several of the customs laboratories and at the Bureau of Standards during November and December, 1917, on various types of apparatus and methods which had been used previous to that time in customs laboratories.

In the main, three types of freezing-point apparatus were investigated at this Bureau, and determinations were made, under various conditions, of the solidification point of pure naphthalene,

pure naphthalene to which other substances had been added, and impure samples which had been submitted to the Bureau.

The three types of apparatus which were designated as Nos. 1, 2, and 3 may be briefly described as follows:

No. 1 was practically the same as the apparatus which will be described later in this paper.

No. 2 consisted of a cylindrical Dewar or vacuum container, 20 cm in depth and 3 cm in internal diameter, in which the test sample was allowed to cool while its solidification point was being observed.

No. 3 consisted of a  $\frac{7}{8}$ -inch test tube containing the sample immersed in a beaker of water which was heated sufficiently to melt the naphthalene and then allowed to cool while the solidification point was being observed.

Comparative measurements made with the three types of apparatus, using pure naphthalene, showed that consistent and accurate results could be obtained with any of them if proper precautions were taken. The results of the comparison are given in Table 1.

TABLE 1.—Averages of Solidification Points Found for a Sample of Pure Naphthalene with Three Types of Apparatus and with Resistance and Mercurial Thermometers.

Apparatus	Platinum resistance thermometer	Mercurial thermometer
	° C	° C
No. 1.....	80.10	80.08
No. 2.....	80.10	80.10
No. 3.....	80.12	80.10

The choice of the apparatus can, from the above results, be seen to depend largely upon the factors of simplicity, convenience, availability, and speed.

Apparatus No. 1 seemed to possess advantages in the above respects sufficient to warrant its adoption.

In the experimental work a platinum resistance thermometer, a mercurial thermometer graduated from 0 to 100° C in 0.2° intervals, and a mercurial thermometer graduated from 70 to 110° C



in  $0.1^{\circ}$  intervals were used. With the long mercurial thermometers the stem correction was large, and for this reason the short thermometer, graduated according to specifications which will be given later, was preferred. Thermometers graduated for partial immersion did not seem desirable.

The effect of adding moisture to the pure sample is given below:

	$^{\circ}\text{C}$
Pure sample naphthalene, solidification point.....	80.13
3 per cent distilled water added, solidification point.....	79.78
Heated one hour at $110^{\circ}$ ; solidification point.....	80.10

This experiment shows very clearly the importance of designing whether or not the sample shall be dried previous to making the solidification point determination if consistent results are to be obtained.

A dry sample exposed to an atmosphere saturated with moisture in a closed vessel for three days showed no change in the freezing point.

## V. DESCRIPTION OF STANDARDIZED APPARATUS AND METHOD

The following is a description of the apparatus and method finally adopted and used at this Bureau for the determination of the solidification point of naphthalene and recommended in the report of the previously mentioned conference. As will be shown later, the method can be used satisfactorily for obtaining the freezing points of paraffins and many other substances.

*Apparatus.*—The form of the apparatus shown in Fig. 1 consists of a  $\frac{7}{8}$ -inch test tube, 7 inches long (a stock size) surrounded by an air jacket which may be formed by a bottle. The bottle is closed by a stopper which supports the test tube. The test tube carries a stopper about  $\frac{7}{8}$  inch thick, with suitable perforations for thermometer and stirrer. The stirrer consists of a loop of glass, with a glass stem, the loop surrounding the thermometer. The test tube, with its jacket, is placed in a water bath. The level of the water in the water bath should be at least as high as the level of the melted naphthalene. A stirrer in the water bath is not necessary.

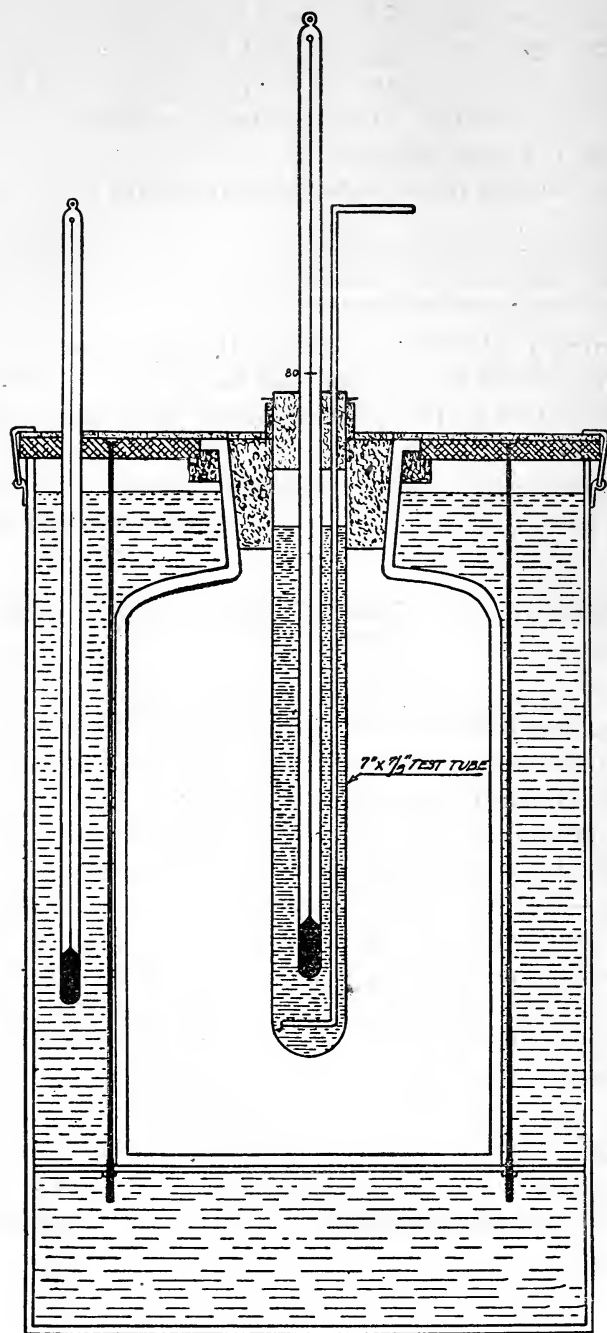


FIG. 1.—Apparatus for determining solidification points

**Thermometers.**—The thermometer used is to be made according to the following specifications. The use of other suitable thermometers—that is, thermometers similar to this but having no ice point—is permissible.

The general appearance of the thermometer is shown in Fig. 2. It is graduated from  $-1^{\circ}$  to  $+1^{\circ}$  and from  $74$  to  $102^{\circ}$  in  $0.1$  intervals.

The required dimensions are: Total length, 33 to 35 cm; diameter of stem, 5.5 to 6.5 mm; length of  $28^{\circ}$  interval from  $74$  to  $102^{\circ}$ , not less than 18 cm; bulb same diameter as stem, or smaller, length not over 4 cm; and the  $80^{\circ}$  mark not less than 14 cm nor more than 16 cm above bottom of bulb.

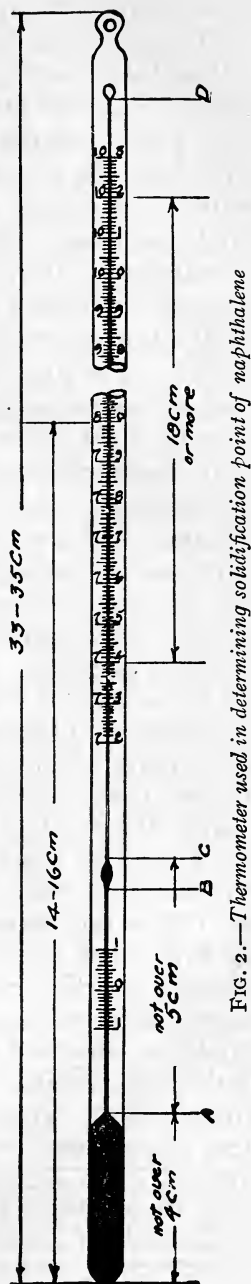
The bulb should be made of suitable thermometric glass, and the stem of enamel-backed thermometer tubing.

The graduation lines should be clear and sharp, and their thickness should be not more than 0.1 of the length of a graduation interval. The longer lines should preferably extend equally to the right and left of the shorter ones. The numbers should be placed as shown in the drawing. The bulb should be thoroughly annealed to prevent change of indications with time.

The manufacturer's name or trade-mark and a serial number should be engraved on the thermometer.

A suitable case, preferably of brass, with a slip or screw cap, should be provided for the thermometer.

The correction at any point of the scale should not exceed  $0.15^{\circ}\text{C}$ , nor should the change in the corrections over any interval exceed 0.5 per cent of that interval. These



requirements apply provided the thermometer is used with bulb and mercury column at the same temperature.

*Procedure.*—(a) Take care to get a representative portion of the sample, break up lumps or moth balls, and mix thoroughly, but avoid loss of volatile matter as much as possible.<sup>3</sup>

(b) Melt the naphthalene by immersing the test tube in water heated to not over 90° C. The level of the melted naphthalene should be about 2 inches below the top of the tube in which it is contained. If a large number of determinations are to be made, a water bath maintained at about 90°, and provided with a suitable support for a number of test tubes, will be found convenient. The naphthalene should not be heated above 90° nor longer than necessary, and the tubes should be kept closed in order to avoid loss of volatile material.

(c) Transfer the naphthalene to the apparatus described above. The temperature of the water bath should be between 70 and 75° and need not be raised during the determination. Insert thermometer and stirrer, which may have been previously warmed. This will raise the level of the melted naphthalene about  $\frac{1}{2}$  inch, and the level should then be about  $\frac{1}{2}$  inch below the stopper (limits of  $\frac{1}{4}$  inch to  $\frac{3}{4}$  inch permissible).

The bottom of the thermometer bulb should be at least  $\frac{1}{2}$  inch above the bottom of the test tube. After the temperature of the naphthalene reaches 81°, take readings every half minute, stirring the naphthalene continuously but not violently. In making the readings estimate to the nearest 0.1 division (0.01°) and take the usual precautions to avoid parallax. Readings may be more easily made with the aid of a magnifying glass; but this is not necessary. The solidifying point corresponds to the first series of five or more readings, during which the temperature remains constant (change not over 0.02°). Usually undercooling will occur, in which case the constant temperature should be observed immediately after the undercooling ceases. If the five readings are not identical, take the average of the five readings. Apply the scale and stem corrections. The stem correction for the thermometer specified and the type

<sup>3</sup> In view of the effect of the presence of water in the sample and of the fact that the water can be easily removed without special refining methods, the conference recommended that the sample be freed from moisture before making the determination, provided such procedure were permissible under the law. In a recent supplement to the Manual of Methods for the Port of New York directions are given for drying the naphthalene previous to the solidification-point determination.

of apparatus used will be small (about  $0.03^{\circ}$ ) and may therefore be determined once for all according to the following formula:

Stem correction equals  $0.00016 N(T-t)$  (centigrade temperatures).

$N$  = number of degrees of mercury column emergent.

$T$  = temperature of bulb.

$t$  = average temperature of emergent mercury column.

(d) Repeat the determination with a fresh portion of the sample. The two determinations should agree within  $0.05^{\circ}$ ; and if they do not, make a third determination. Average the results.

It is to be noted that in the above procedure there has been incorporated what is virtually a definition of the solidification point, namely, the temperature at which solidification begins. This definition was adopted by the conference because the determination of the solidification point is essentially a criterion of purity, and it is the depression of the initial freezing point below that of the pure substance which is a measure of the amount of impurity present.

Recommendations substantially the same as the above were submitted to six customs laboratories in various cities, and a cooperative test was made by these laboratories and the Bureau on three samples of naphthalene.

The original samples were received at this Bureau, and subsamples were carefully taken from each. These subsamples were then sent to the different laboratories along with thermometers made according to the specifications previously noted. These thermometers were tested at the Bureau for scale errors before sending to the various offices.

The solidification points obtained at the various laboratories and at this Bureau are given in Table 2.

TABLE 2.—Solidification Points of Three Samples of Naphthalene as Measured at Six Customs Laboratories and at the Bureau of Standards

Sample number	Bureau of Standards	I	II	III	IV	V	VI
	$^{\circ}\text{C}$	$^{\circ}\text{C}$	$^{\circ}\text{C}$	$^{\circ}\text{C}$	$^{\circ}\text{C}$	$^{\circ}\text{C}$	$^{\circ}\text{C}$
D 867.....	79.80	79.70	79.83	79.78	79.87	79.81	(a)
D 723.....	79.51	79.34	79.52	79.53	79.58	79.51	79.60
D 460.....	79.24	79.00	(a)	79.30	79.33	79.38	79.30

a No sample supplied.

It can be seen that the results obtained at the various laboratories and at the Bureau are in good agreement except those reported for laboratory No. I. The low results of No. I may be explained by the fact that a smaller amount of naphthalene than that required in the specifications was used. This laboratory failed to receive a copy of the conference report and used a method which differed in some essential details from that specified.

The agreement of the various laboratories would indicate that determinations of the solidification point of naphthalene in the neighborhood of  $79^{\circ}\text{C}$  are reproducible by this method to  $0.1$  or  $0.2^{\circ}\text{C}$ . The experiments of the Bureau have shown that for naphthalene of higher purity the freezing points of samples can be repeated to  $0.05^{\circ}$  or better.

## VI. SOLIDIFICATION POINT OF PARAFFIN

This same method and apparatus with slight modifications of thermometer and temperature of outer bath were used for paraffin freezing-point determinations. The results are given in Table 3.

TABLE 3.—Determinations of Solidification Points of Three Samples of Paraffin

Designation	Temperature outer bath	Reading <sup>a</sup>	Correction	Solidification point
	$^{\circ}\text{C}$	$^{\circ}\text{C}$	$^{\circ}\text{C}$	$^{\circ}\text{C}$
Sample 1.....	40	54.5	+0.8	55.3
	40	54.5	+ .8	55.3
	40	54.6	+ .8	55.4
	38	54.6	+ .8	55.4
				55.35
Sample 2.....	47	53.8	+ .8	54.6
	46	53.8	+ .8	54.6
	43	53.8	+ .8	54.6
	43	53.8	+ .8	54.6
				54.6
Sample 3.....	36	48.2	+ .8	49.0
	36	48.3	+ .8	49.1
	35	48.2	+ .8	49.0
	35	48.3	+ .8	49.1
				49.05

<sup>a</sup> The average reading over a period of about two minutes, during which temperature remained constant to  $0.1^{\circ}$ .

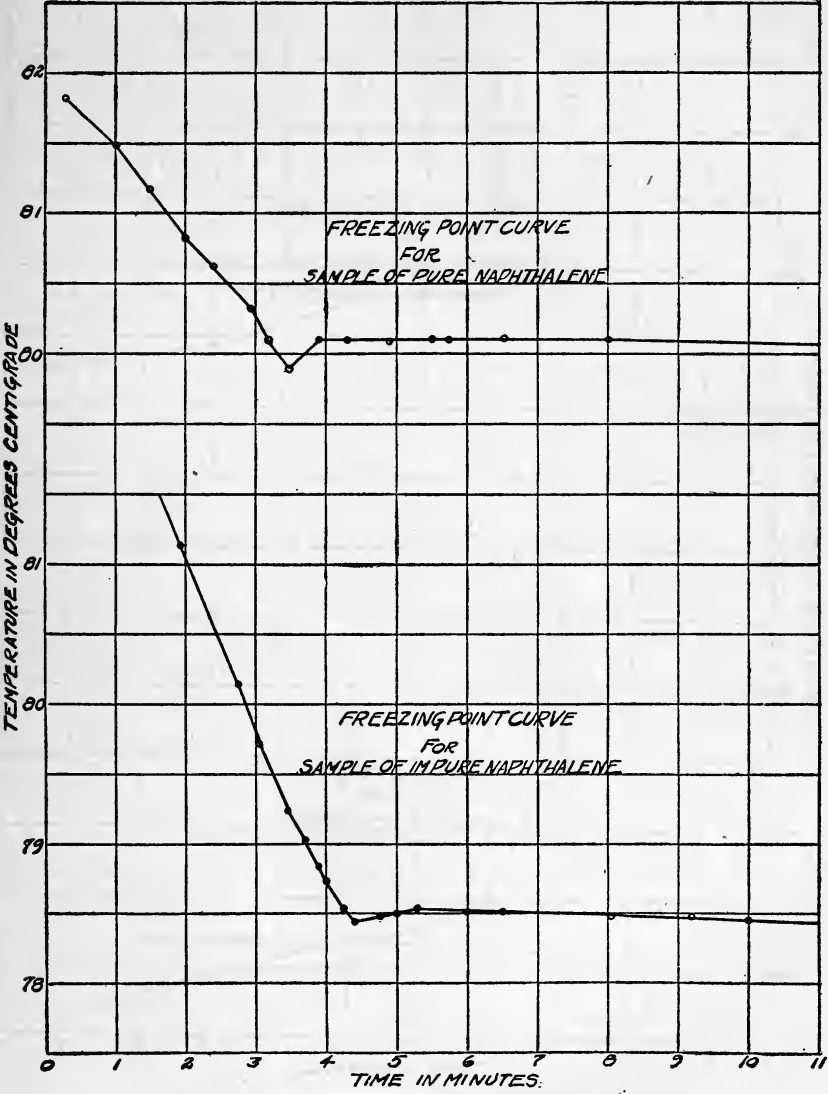


FIG. 3.—Solidification curves for naphthalene

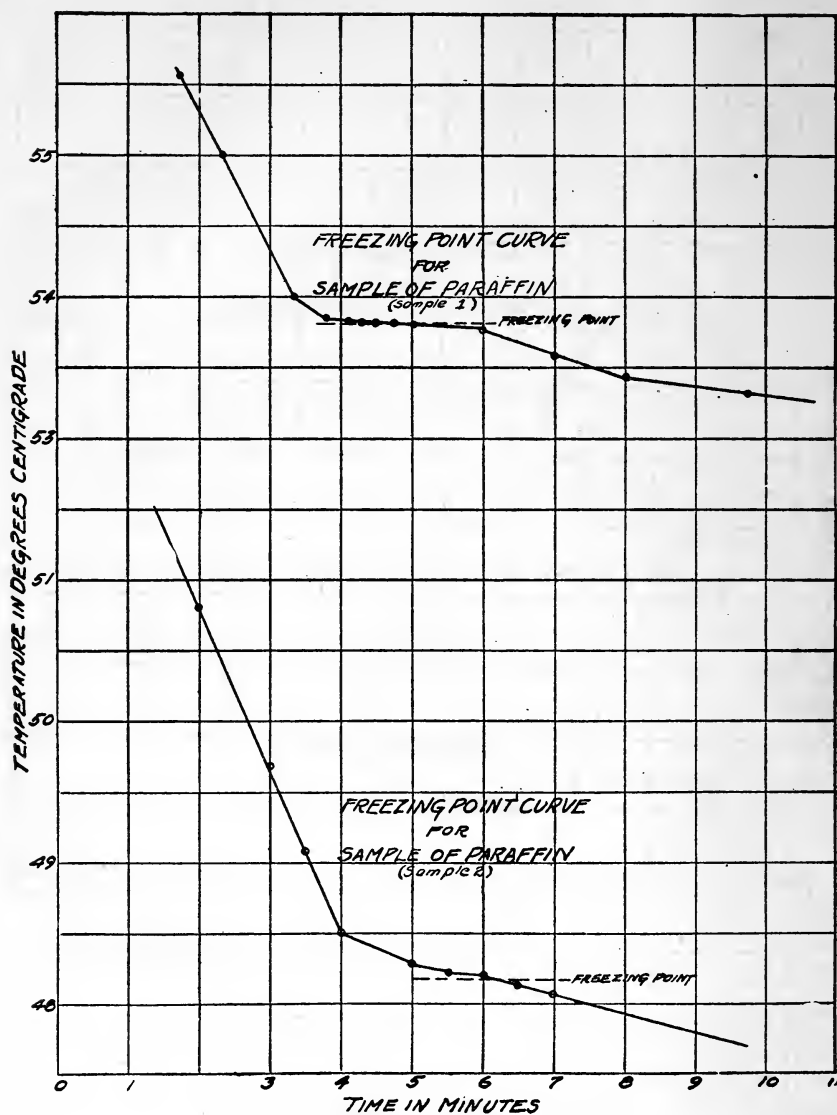


FIG. 4.—Solidification curves for paraffin



The above results indicate that the determination of the solidification point of paraffin may be obtained with the apparatus described to an accuracy of about  $0.1^{\circ}$  or better.

The most desirable thermometer for paraffin freezing-point determinations would be one graduated from  $40$  to  $70^{\circ}$  C or higher in  $0.1$  or  $0.2^{\circ}$  intervals.

If such a special thermometer is not available, consistent and accurate results can be obtained with other suitable thermometers, provided allowance is made for scale error and error due to the emergent mercury column.

In paraffin the undercooling preceding solidification is scarcely observable. The constant-temperature phenomenon is also not as marked as in naphthalene, since paraffin is a mixture and the composition of the liquid changes as solidification proceeds. These experiments, however, have shown that, in general, the temperature will stay constant to within  $0.1^{\circ}$  for about two minutes if the apparatus described is used.

Some typical freezing-point curves of naphthalene and paraffin are shown in Figs. 3 and 4.

This method has been applied in the laboratory to the determination of the solidification points of benzoic acid and also of antifreezing solutions, brines, fire-extinguishing liquids, etc., by the substitution of a cold bath, maintained at a suitable temperature, for the heated water bath.

## VII. SUMMARY

After a brief treatment of the definitions of melting and freezing points, both of pure substances and of mixtures, a method of making solidification-point determinations is described. This method, which is an adaptation of a well-known one, was recommended at a conference of Bureau of Standards and United States customs officials and was adopted by the U. S. Customs Service for the determination of the solidification point of naphthalene. The method has been applied to the determination of the freezing points of many other substances.

WASHINGTON, February 14, 1919.

